Summary.

The results obtained in this research may be very briefly summarized as follows:

I. From the surface tensions by the drop-weight method, of *twenty-four* homogeneous mixtures in various proportions and at two temperatures, it was found that *ten* follow rigidly the law of mixtures in the form $P_{\text{Mix.}} = l_aP_a + l_bP_b +$ etc. (where the summation of the relative weights l_a, l_b, etc., is equal to 1 g.). Of these mixtures, *six* were of two constituents, *two* of three, *one* of four, and *one* of five.

II. Whenever variations appear (the other *fourteen* mixtures) the observed value is invariably less than that calculated from the law. These deviations increase in magnitude with increased temperature, and are always at a maximum at both temperatures for that mixture which contains equal weights (in g.) of the constituents.

III. Although the deviations might be due to the magnitude of the difference in the surface-tension values of the constituents when pure, the effect is probably negligible and merges into the more important factor—the nature of the constituent. An example of this latter is chlorobenzene, which renders every mixture, in which it is, abnormal. The deviation of a complex mixture is not a summation of the deviations of the pairs of liquids of which it could be made, but is of the same order as these.

IV. It is shown that chemical interaction for binary mixtures could not be the cause of the maximum deviation invariably found at a composition of mixture of 50% by weight (in g.) of the two constituents—whereas this behavior is shown to be exactly that which might be expected if the one liquid by its simple, physical, presence influenced the value of the property of the other (or each affected the other), and the conclusion is consequently drawn that the mixture law considered is a rigid law, provided no chemical interaction takes place between the constituents, and neither liquid influences the value of the property of the other. The effect of this latter action is invariably to produce the maximum deviation at a 50% mixture by weight (in g.) of the two constituents.

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THE PROPERTIES OF MIXED LIQUIDS. IV. THE LAW OF MIXTURES. II.

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This investigation is a continuation of the work of Morgan and Griggs,[1]

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[1] See preceding paper.

with the object of showing the various possible results obtainable from the form of the mixture law employed by them.

The experimental work of the research consists in the determination of the surface tensions, by the drop-weight method, of the various pure liquids at a number of temperatures, and of their binary admixtures in various proportions at the same temperatures.

The dropping tip used in this work fulfilled all the conditions necessary for the exact holding of the proportionality of drop weight and surface tension, *i. e.*, the drop profile from it was normal with all the liquids and mixtures studied. The factor of proportionality was determined by aid of benzene at three temperatures,[1] each drop-weight value being the mean of at least three sets of thirty-drop determinations with five-drop blanks, the values being concordant to within a few hundredths of 1%. The results, which by their comparison led to this factor of proportionality, are given in Table I, the values of the surface tension of benzene being calculated from the equation

$$\gamma_{t,\mathrm{C_6H_6}} = 30.514 - 0.1321t + 0.000082t.^2$$

TABLE I.

Standardization of the Tip.

	Benzene.		
t.	Wt. 1 drop mg. (w).	Surface tension in dynes per cm. (γ).	Constant ($= \gamma/w$).
25	28.372	27.263	0.9609
30	27.710	26.625	0.9608
35	27.056	25.991	0.9606
		Average,	**0.9608**

To find the surface tension of any (proper) liquid in dynes per cm., from the weight (in mg.) of a drop falling from this tip at the same temperature, we have, then, the relationship

$$\gamma_{l,t} = 0.9608 \times w_{l,t}.^2$$

Purification of the Liquids, and Preparation of the Mixtures.

The liquids used in this work were all carefully purified, and whenever a new supply of liquid was necessary, its surface tension was redetermined before it was used in a mixture.

The benzene employed was purified according to the method of Richards and Shipley.[3] The portion distilling at 80.1° (corr.) was then crystallized and used.

The acetone was allowed to stand over calcium chloride for a day and distilled, and then allowed to stand over anhydrous copper sulfate for a

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[1] See Morgan, THIS JOURNAL, **37**, 1462 (1915).

[2] From the value of the constant 0.9608, the mean diameter of this tip is calculated to be 5.20 mm. (see Morgan, *Loc. cit.*).

[3] THIS JOURNAL, **36**, 1825 (1914).

week and redistilled. The portion distilling at 56.3° (Bar. = 760.6) was used. A second distillation here led to the same drop weight as the first, and is therefore probably unnecessary. To check the purity of this sample, its density was determined by aid of an Ostwald-Sprengel pycnometer, with stoppered limbs. The values obtained were

$$d_{20/4} = 0.79170 \text{ and } d_{25/4} = 0.78598.$$

The value at 20° is to be compared with the following results obtained by previous investigators: Eisenlohr,[1] 0.7910; Brühl,[2] 0.7912; Lowry,[3] 0.7920. The refractive index was also determined of this sample, using a Zeiss-Pulfrich refractometer. The result at 20°, with the sodium line, was 1.35934, where previously found values were Eisenlohr,[4] n^{20}_{D} 1.35931; Korten,[5] $n^{19.4}_{D}$ 1.35886.

The ethyl alcohol employed was originally a sample of 99.8% purity. A further distillation over quicklime was made, after which the surface tension was found to be identical with that found by Morgan and Neidle[6] for their most carefully and repeatedly purified sample.

The phenol was especially prepared[7] and was further purified by distilling three times under reduced pressure, the distillate being recrystallized. The surface-tension values of this sample agreed perfectly with those found by Morgan and Egloff[8] and by Morgan and Evans[9] in this laboratory, who used the same method of purification.

The water employed was prepared by twice redistilling distilled water, first with alkaline permanganate through a glass condenser, and then, after addition of a small amount of phosphoric acid, through block tin.

The acetic acid was purified by recrystallization until a constant drop weight was found. The surface tensions found here agree perfectly with those of Morgan and Neidle.[4]

The various mixtures of liquids investigated were made up in the following manner: To a weighed amount of the less volatile constituent in a small Erlenmeyer flask, fitted with a thoroughly rolled cork stopper, such a volume of the other liquid was added as to give approximately the concentration desired, the exact concentration then being found by the weighing of the stoppered flask and its contents. Although many of these solutions were found to exhibit the same surface tension, and therefore the

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[1] *Z. physik. Chem.*, **75**, 587 (1910).

[2] *Ann.*, **200**, 139 (1880).

[3] *J. Chem. Soc.*, **105**, 81 (1914).

[4] *Loc. cit.*

[5] Dissertation, Bonn (1890).

[6] THIS JOURNAL, **35**, 1857 (1910).

[7] By the Hoffman and Kropff Chemical Company.

[8] THIS JOURNAL, **38**, 844 (1916).

[9] *Ibid.*, **39**, 2151 (1917).

same concentration, for several days after preparation, to avoid all possibility of error, only those measurements were considered reliable which were made on the same day on which the solution was prepared.

Approximately 20 g. of each solution were prepared, and as they could be weighed accurately to within 5 mg., the concentrations can be regarded as accurate to about 0.02%. Solutions such as have been used in this work would not differ by as much as 0.001 dyne for such a change in concentration. The operation of transferring solutions from the container to the supply vessel of the drop-weight apparatus required only a fraction of a minute, and any change in concentration due to that was shown to be negligible.

Experimental Results.

The surface tensions marked "obs.," given in the following tables have all been directly determined in this work; the significance of the other captions will be discussed later.

TABLE II.—SURFACE TENSION OF ACETONE-WATER MIXTURES.[1]

% = g. Acetone per 100 g. of Mixtures.

%.	$\gamma_{0°}$ obs.	$\gamma_{0°}$ calc.	Dev.	$\gamma_{25°}$ obs.	$\gamma_{20°}$ calc.	Dev.
0	75.87	...	...	71.86	...	...
5	58.80	73.33	—14.53	54.54	69.37	—14.83
10	52.25	70.80	—18.55	47.81	66.89	—19.08
20	43.98	65.73	—21.75	39.83	61.92	—22.09
25	41.06	63.20	—22.14	36.98	59.43	—22.45
30	38.73	60.66	—21.93	34.73	56.95	—22.22
40	34.94	55.59	—20.65	31.50	51.98	—20.48
50	32.32	50.52	—18.20	29.25	47.01	—17.76
75	28.50	37.84	— 9.34	25.75	34.59	— 8.84
85	27.46	32.77	— 5.31	24.63	29.62	— 4.99
90	26.92	30.24	— 3.32	24.08	27.14	— 3.06
95	26.23	27.70	— 1.47	23.19	24.65	— 1.46
100	25.17	...	...	22.17	...	...

%.	$\gamma_{45°}$ obs.	$\gamma_{45°}$ calc.	Dev.
0	68.46	...	...
5	51.52	66.03	—15.49
10	44.67	63.59	—18.92
20	36.87	58.72	—21.85
25	34.00	56.29	—22.29
30	31.98	53.86	—21.88
40	28.94	48.99	—20.05
50	26.81	44.12	—17.31
75	23.54	31.95	— 8.41
85	22.40	27.08	— 4.68
90	21.79	24.65	— 2.86
95	20.89	22.21	— 1.32
100	19.78	...	...

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[1] The surface tension of the purified acetone was determined at six different tem-

TABLE III.—SURFACE TENSION OF ACETONE-ETHYL ALCOHOL MIXTURES.
% = g. Ethyl Alcohol per 100 g. of Mixture.

Temp. = 20°.

%.	γ obs.	γ calc.	Dev.
00.00	22.776	....	...
15.02	22.633	22.589	+0.044
20.03	22.598	22.527	+0.071
29.94	22.506	22.402	+0.104
40.06	22.406	22.278	+0.128
50.03	22.302	22.155	+0.147
59.94	22.175	22.032	+0.143
79.70	21.910	21.786	+0.124
90.02	21.752	21.658	+0.094
100.00	21.534	....	...

Temp. = 0° C.

%.	γ obs.	γ calc.	Dev.
00.00	25.192	....	...
50.00	24.297	24.141	+0.156
100.00	23.090	....	...

Temp. = 45° C.

%.	γ obs.	γ calc.	Dev.
00.00	19.781	....	...
50.00	19.831	19.685	+0.146
100.00	19.589	....	...

TABLE IV.—SURFACE TENSION OF PHENOL-ACETONE MIXTURES.
% = g. Acetone per 100 g. of Mixture.

%.	$\gamma_{35°}$ obs.	$\gamma_{35°}$ calc.	Dev.
00.00	38.033	....	...
38.47	30.465	31.462	—1.062
49.73	28.001	29.539	—1.538
60.01	26.141	27.783	—1.642
65.01	25.257	26.929	—1.672
70.03	24.423	26.072	—1.649
74.96	23.701	25.230	—1.529
100.00	20.953	....	...

%.	$\gamma_{0°}$ obs.	$\gamma_{0°}$ calc.	Dev.
00.00	41.701	....	...
59.98	30.24	31.78	—1.54
64.60	29.44	31.02	—1.58
70.78	28.48	30.00	—1.52
100.00	25.17	....	...

peratures, and an equation found to fairly represent it by the method of least squares. The results are given in the table below:

Acetone.

t.	γ (obs.).	γ (calc.).
0°	25.192	25.172
15	23.366	23.375
25	22.163	22.177
35	20.953	20.979
45	19.784	19.781
55	18.597	18.583

$$\gamma_t = 25.172 - 0.1198t.$$

TABLE V.—SURFACE TENSION OF PHENOL-ETHYL ALCOHOL MIXTURES.

% = g. Ethyl Alcohol per 100 g. of Mixtures.

%.	γ_{35° obs.	γ_{35° calc.	Dev.
00.00	38.033	....	...
25.39	32.120	33.547	—1.427
49.44	27.148	29.299	—2.151
55.82	26.038	28.172	—2.134
59.68	25.415	27.490	—2.075
74.60	23.190	24.854	—1.664
100.00	20.367	....	...

%.	γ_{0° obs.	γ_{0° calc.	Dev.
00.00	41.701	....	...
50.20	30.23	32.36	—2.13
55.82	29.22	31.31	—2.09
59.73	28.52	30.58	—2.06
74.60	26.18	27.82	—1.64
100.00	23.090	....	...

TABLE VI.—SURFACE TENSION OF BENZENE-ACETIC ACID MIXTURES.

% = g. Acetic Acid per 100 g. of Mixture.

%.	γ_{30° obs.	γ_{30° calc.	Dev.
00.00	26.625	....	...
10.27	26.09	26.53	—0.44
25.10	25.62	26.40	—0.78
38.89	25.30	26.27	—0.97
49.77	25.10	26.16	—1.06
59.95	24.988	26.077	—1.089
61.48	24.969	26.063	—1.094
62.90	24.961	26.050	—1.089
75.42	25.05	25.94	—0.89
100.00	25.711	....	...

%.	γ_{15° obs.	γ_{15° calc.	Dev.
00.00	28.551	....	...
55.13	26.849	27.792	—0.943
60.40	26.729	27.720	—0.991
65.20	26.714	27.654	—0.940
100.00	27.175	....	...

TABLE VII.—SURFACE TENSION OF BENZENE-ETHYL ALCOHOL MIXTURES.

% = g. Ethyl Alcohol per 100 g. of Mixture.

%.	γ_{25° obs.	γ_{25° calc.	Dev.
00.00	27.263	....	...
16.70	25.542	26.241	—0.70
20.04	25.281	26.037	—0.756
22.82	25.104	25.867	—0.763
25.04	24.971	25.731	—0.76
50.06	23.651	24.200	—0.55
75.04	22.402	22.672	—0.27
100.00	21.145	....	...

TABLE VII (*continued*).

%.	γ_{45° obs.	γ_{45° calc.	Dev.
00.00	24.735	....	...
19.96	23.124	23.708	—0.584
25.00	22.859	23.448	—0.589
29.83	22.633	23.197	—0.564
100.00	19.589	....	...

TABLE VIII.—SURFACE TENSION OF BENZENE-METHYL ALCOHOL MIXTURES.

% = g. Methyl Alcohol per 100 g. of Mixture.

%.	γ_{30° obs.	γ_{30° calc.	Dev.
00.00	26.625	....	...
15.04	25.188	25.788	—0.600
20.06	24.804	25.508	—0.704
25.10	24.510	25.226	—0.716
30.13	24.235	24.948	—0.713
50.04	23.270	23.839	—0.569
75.15	22.125	22.440	—0.315
100.00	21.058	....	...
%.	γ_{0° obs.	γ_{0° calc.	Dev.
00.00	30.514	....	...
19.94	28.143	29.144	—1.001
25.00	27.779	28.796	—1.017
30.07	27.440	28.448	—1.008
70.07	25.211	25.699	—0.488
100.00	23.643	....	...

TABLE IX.—SURFACE TENSION OF ACETONE-METHYL ALCOHOL MIXTURES.

% = g. Methyl Alcohol per 100 g. of Mixture.

%.	γ_{30° obs.	γ_{30° calc.	Dev.
00.00	21.578	....	...
33.25	21.775	21.405	+0.370
39.88	21.747	21.371	+0.376
49.92	21.689	21.318	+0.371
100.00	21.058	....	...
%.	γ_{0° obs.	γ_{0° calc.	Dev.
00.00	25.192	....	...
33.25	25.088	24.677	+0.411
39.88	25.004	24.574	+0.430
49.84	24.877	24.420	+0.457
59.83	24.673	24.265	+0.408
100.00	23.643	....	.....

TABLE X.—SURFACE TENSION OF METHYL ALCOHOL-ETHYL ALCOHOL MIXTURES.

% = g. Methyl Alcohol per 100 g. of Mixture.

Temp. = 0° C.

%.	$\gamma_{obs.}$	$\gamma_{calc.}$	Dev.
0.00	23.090	....	.....
50.45	23.395	23.367	+0.028
100.00	23.643	....	.....

TABLE X (*continued*).

%.	$\gamma_{obs.}$	$\gamma_{calc.}$	Dev.
	Temp. = 30° C.		
00.00	20.756	.....	.....
50.45	20.909	20.908	+0.001
100.00	21.058	....	.....
	Temp. = 50° C.		
00.00	19.200	....	.....
50.45	19.235	19.323	—0.088
100.00	19.446	....	.....

TABLE XI.—SURFACE TENSION OF BENZENE-PHENOL MIXTURES.

% = g. Benzene per 100 g. of Mixture.

%.	$\gamma_{35°}$ obs.	$\gamma_{35°}$ calc.	Dev.
00.00	38.033	....	.....
24.86	32.513	35.037	—2.524
29.88	31.764	34.433	—2.669
35.18	31.038	33.795	—2.757
39.03	30.561	33.333	—2.772
45.00	29.892	32.614	—2.722
50.11	29.400	31.997	—2.597
100.00	25.991	....	.....

Discussion of the Results.

The following systems of mixed liquids have been studied in this work: *Water-acetone, acetone-ethyl alcohol, acetone-phenol, phenol-ethyl alcohol, benzene-acetic acid, benzene-ethyl alcohol, benzene-methyl alcohol, acetone-methyl alcohol, methyl-alcohol-ethyl alcohol*, and *benzene-phenol.*

In the tables of results, the surface tensions of the pure constituents, at the temperature in question, are given opposite the numbers 0 and 100 in the column denoting percentages, *i. e.*, g. of the one constituent in 100 g. of the mixture. The surface tensions observed directly for the various mixtures are given in the next column, under the caption "γ obs.," while the values under "γ calc." are calculated on the basis of the mixture law, as used by Morgan and Griggs, which may be written

$$\gamma_{Mixt.} = \gamma_1 x + \gamma_2 (1 - x),$$

where x and $1 - x$ are the fractional g. of the two constituents in every g. of the mixture, and γ_1 and γ_2 are the surface tensions of the constituents when in the pure state, at the temperature of the mixture. The *deviation from this mixture law, i. e.*, the difference between the observed and calculated values of γ, is then given for each mixture under the caption "deviation."

The plots given for some of the systems, Figs. 1 to 12, include the property-composition curve; the straight line representing the following of the mixture law; and the curve of the deviation of the observed property from the mixture law, plotted against the composition of the mixture.

This latter enables one at a glance to find the concentrations in grams of constituents of the mixture leading to the maximum deviation, and also shows the sharpness of that maximum.

According to the theory of Denison,[1] the concentrations of the constituents, at which the deviation from the mixture law is a maximum, indicate the relative proportions of the constituents in the compound formed by the two liquids.

Even if there were no theoretical grounds for this method of treatment, it must remain a most important empirical fact that a liquid mixture (which, in respect to the value of a property itself, perhaps shows a continuous change with changing composition, therefore exhibiting no maximum or minimum value in the so-called property-composition curve) exhibits at some point a maximum deviation of the observed value of the property from the value calculated from the mixture law. This is all the more striking when we compare this maximum deviation from the mixture law with a maximum or a minimum of the property-composition curve, when one of these is present, for these invariably shift in respect to concentration with a change in temperature, whereas the maximum deviation at all temperatures remains invariably at the same concentration.

An experimental test of the deviation of property-composition theory most likely to exhibit its shortcomings, if it has them, is one that would show that the relative concentrations of the liquids exhibiting the maximum deviation (and hence that taken as the composition of the compound formed) does not represent exact *molecular* proportions, or that it would represent a compound of a very complicated character. The limited work of Morgan and Davis and of Morgan and Egloff[2] in this field, as well as the more extended work of this investigation, however, has shown that in no case is the compound indicated of other than a perfectly simple and plausible formula; and yet it might be justly said that the deliberate intent in all this work has been to discover just such inconsistencies, if they exist.

It is just such a test as this that indicates most clearly and so often the usual lack of significance of a maximum or minimum in the property-composition curve, *i. e.*, of the relative concentrations of the constituents which lead to a maximum or minimum value of the property itself. This contrast in behavior, indeed, accentuates the significance of the relative concentrations corresponding to a maximum deviation of the observed property from that calculated by the mixture law, which has passed all such tests satisfactorily thus far. The above would naturally cause this method of treatment, even considered as a purely empirical thing, to assume extraordinary significance.

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[1] *Trans. Faraday Soc.*, 8, 20, 35 (1912).

[2] Nos. 1 and 2 of this series of papers.

Perhaps the best way to summarize the above experimental results in general and in few words, is the following: *The maximum deviation of the value of the property (surface tension) as observed from that calculated by the mixture law (using g. as the relative weights) is invariably found to exist at a concentration of the mixture corresponding to a definite and simple molecular proportion of the constituents, and this same concentration continues to exhibit the maximum deviation at all temperatures.*

It is to be remembered in this connection, however, that no indication is given of the *actual* molecular weight of the compound by this method, but only of the *relative* proportions of the constituents in terms of molecular weight, which exist in that compound. We could not distinguish, for example, by this method, between a compound such as A_2B and A_4B_2, *i. e.* $(A_2B)_2$.

The fact that the maximum deviation of a *physical* property always appears just at a certain concentration of the constituents, which is expressible in terms of an even number of molecular weights of these, even empirically must suggest the conclusion *that some chemical process, the formation of a compound, for example, in just those proportions is responsible for the presence of the maximum.* Most assuredly it is a very significant linking together of physical and chemical properties.

We shall now consider in the sequence given above, the details of the individual systems themselves, calling attention to the compounds formed, according to the above theory, and to the striking characteristics of the specific data.

A very complete and exhaustive study (at every 5% from 0 to 100, each at three temperatures, 0°, 25° and 45°) of the system *acetone–water* was undertaken, for the reason that no complete survey of any physical property, as it changes with changing concentrations, is to be found in the literature. The property-composition curve for this system (Fig. 1) is without maxima or minima, and indicates the large depressing effect on the surface tension of additions of acetone to water. However reminiscent of the curve for a system of mutually soluble liquids of the type phenol–water, it will be noted that in one particular this curve is quite different; for in the former practically all the effect is produced by the addition of about 8% of phenol, the surface tension between this and 100% varying but slightly from that of phenol itself.

A study of the deviation-composition curve (Fig. 2) indicates most plainly that the maximum deviation corresponds to a concentration of acetone lying between 24 and 25 g. in 100 g. of the mixture, and remains at the same concentration at 0° as at 45°, according to Table II. The simplest compound of acetone and water of these relative proportions is $(CH_3)_2CO.10H_2O$, corresponding to 24.37% acetone. This is the only compound indicated by surface tension, but, naturally, that only means that this compound has a different and greater effect of surface tension than any other. It is possible, of course, that another physical property, while indicating another compound, if such exist, would fail to indicate this one, owing to the fact that it fails to alter this property.

Expressed purely in terms of experiment, the work on this system indicates that the maximum deviation of the observed surface tension from that calculated by the mixture law is found for that mixture which contains 1 mol of acetone to every 10 mols of water.

The mixture of *acetone* and *ethyl alcohol* is composed of liquids differing less in surface tension than was the case in the previous system, the largest difference, that at 0°, being something over 2 dynes per cm. The deviations here (see Table III) are not sufficiently large, however, to warrant the application of the deviation-composition theory. It is to be observed in this case that, just as was noted by Morgan and Griggs in so many cases, the maximum deviation would come at what is practically 50% by weight in g. of the two constituents. Contrary to any case found by them, however, the deviations here are invariably positive, *i. e.*, the observed value is *larger* than that calculated by the mixture law.

A curious fact noticeable with this system is that the observed value of the surface tension at a 50% mixture at 45°, but not at 0°, *is larger than that of either constituent*, although at this point the individual values of γ of the constituents differ but slightly, *viz.*, 19.781 and 19.589, that of the mixture being 19.831. The only other system giving similar results is that of sulfuric acid and water[1] where, however, the deviations were large enough for the application of the theory, and the maximum was found at a different percentage than 50.

The only conclusion possible here is that if any reaction to form a compound takes place between the constituents, it does not change the surface tension very noticeably, for the maximum deviation is less than 0.15 dyne per cm. The significance of the *positive* deviations, and of the value of the mixture being larger than that of either constituent alone is at present not apparent. The maximum deviation for the 50% by weight mixture, on the other hand, is most probably due, as was assumed by Morgan and Griggs for similar cases where the deviation was negative, to the effect of the *physical* contact of one liquid on the other, which would naturally be at a maximum at just this concentration, *i. e.*, where the liquid changing, and that causing the change, are *both* at a maximum concentration in grams.

The system *phenol–acetone* is one in which the constituents differ in surface tension by as much as 16.5 dynes per cm. Notwithstanding this, however, the deviations are not large (1.67 at greatest), although as will be seen from Fig. 4 they indicate a very plain maximum at a concentration

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[1] See Morgan and Davis, *Loc. cit.*

FIG I

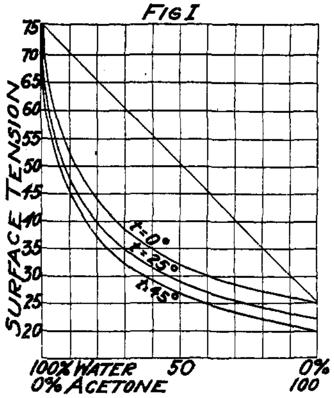


FIG 2

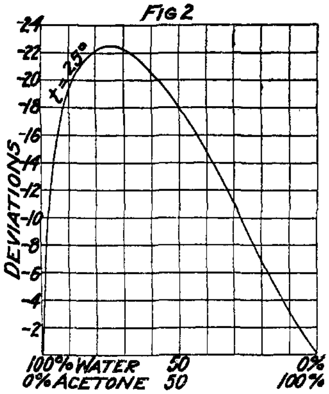


FIG 3

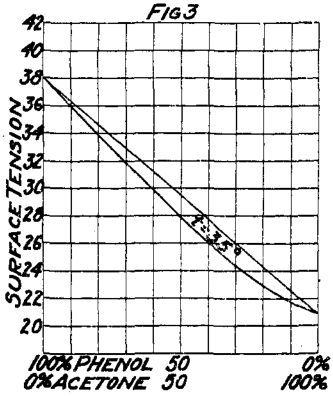


FIG 4

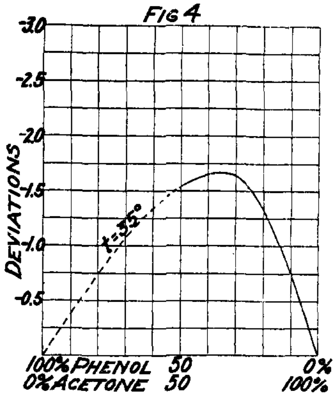


FIG 5

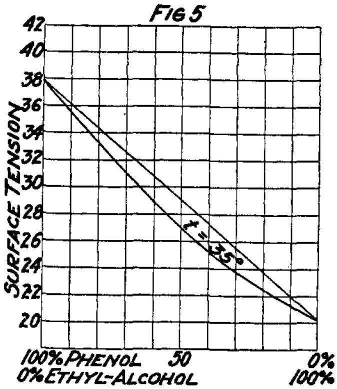


FIG 6

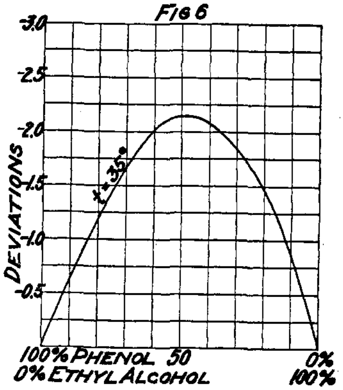


FIG 7

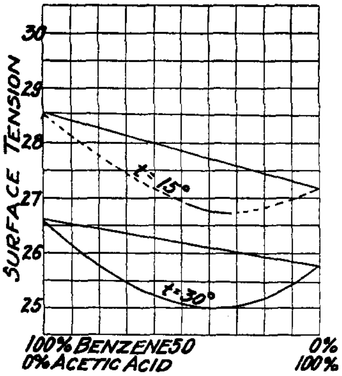


FIG 8

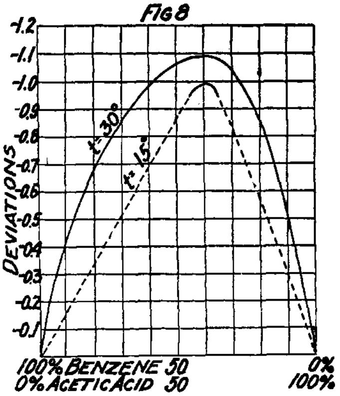


FIG 9

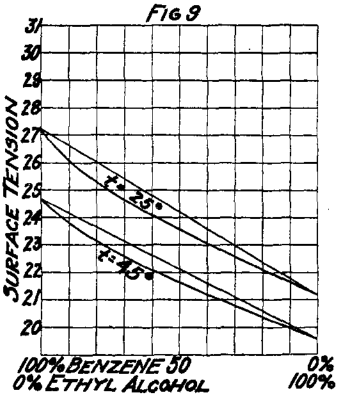


FIG 10

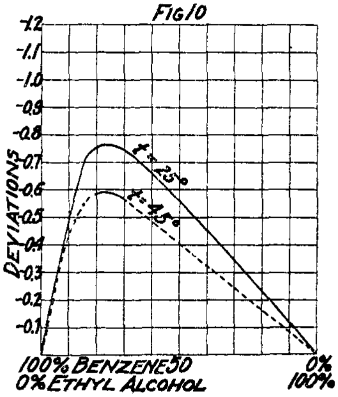


FIG 11

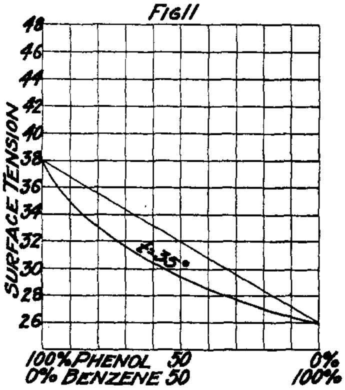
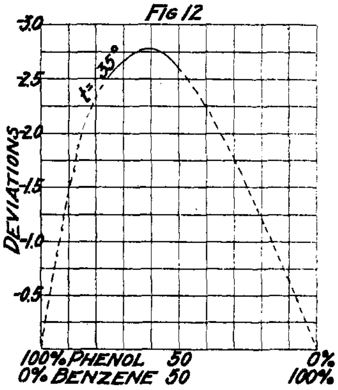


FIG 12



of just about 65% of acetone at both 0° and 35°. As the compound $C_6H_5OH.3(C_3H_6O)$ represents 64.93% of acetone, this is the one evidently formed according to the deviation-composition theory.

Schmidlin and Lang[1] by phase-rule methods have succeeded in isolating a compound of these liquids of the formula $2C_6H_5OH.(CH_3)_2CO$, the melting point of which is 14.8°. It is evident from the surface-tension results that if such a compound is present in the liquid state, its surface tension does not distinguish it from the constituents, or from the compound indicated by these results, while the one found above does not exist as a solid.

Bramley[2] has determined the densities of various mixtures of these liquids at 20.05°, and it is of interest to note that his results indicate a maximum deviation from the mixture law for densities between 64.93% and 73.28%, the two concentrations nearest to our 64.93, which may be taken as satisfactory confirmation, using another physical property, of the surface-tension conclusion.

Expressed experimentally, the maximum deviation of both surface tension and density, from the mixture law, at all temperatures is at just that concentration of constituents which corresponds to one molecular weight of phenol to every three molecular weights of acetone.

The system *phenol–ethyl alcohol* exhibits a property-composition curve similar to that of phenol and acetone. The deviations are larger here, however, and attain a maximum in the near vicinity of 50% of ethyl alcohol. The compound $C_6H_5OH.2C_2H_5OH$ would correspond to 49.47% of alcohol, and hence is that indicated by surface tension on the basis of the deviation-composition theory.

This is the first system leading to a maximum deviation around a concentration of 50% by weight of the constituents, which presents a deviation (2.151) large enough to warrant the application of the deviation-composition theory. It is also the first for which a 50% concentration would correspond to an even molecular formula. It is merely a coincidence, then, that would make it seem to belong to the same class as those studied by Morgan and Griggs, and as the acetone-ethyl alcohol above, and should in no way affect the reasoning in those cases.

One of the most interesting of the systems studied in this work is that composed of *benzene* and *acetic acid*, for the reason that it has also been studied by both the freezing point and coefficient of distribution methods. Fig. 7 shows the property-composition curve and Fig. 8 that of deviation-composition. Here at both temperatures (15° and 30°) the maximum deviation is found at a composition of 60% by weight of acetic acid.

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[1] *Ber.*, **43**, 2812 (1910).

[2] *J. Chem. Soc.*, **109**, 10 (1916).

The composition of the compound $C_6H_6.2(CH_3COOH)$ corresponds to 60.6% acetic acid, and hence is the one indicated here.

The viscosities of Dunstan[1] for this system show the maximum deviation at 25° (from an assumed mixture law for viscosity) to lie between 65.07% and 51.71% the two nearest to 60% of acetic acid, and considerably nearer the former than the latter, which can only be considered as confirming the surface-tension result.

It is to be especially noted in this connection that acetic acid has long been known, from freezing-point determinations, to exist in the form of double molecules when dissolved at a low concentration in benzene (see, for example, Beckmann[2]). Naturally, this same conclusion would have been drawn if instead of simply forming double molecules, these two molecules of acetic acid had united with one molecule of benzene, the solvent; for the removal of this small amount of benzene from its role of solvent would not have caused, in weak solutions, an appreciable difference in the freezing-point results. Of course, this is a possibility in the case of any weak solution, and must be considered as a serious factor when any other method indicates not only a polymerization of solute, but the combination of that aggregate with an amount of the solvent.

The same form of reasoning is, of course, applicable to the result obtained from distribution experiments of acetic acid between benzene and water[3] which again plainly indicates the existence of double molecules of acetic acid in benzene. Here again no appreciable difference in the experimental result, at low concentrations, would have been observed, if instead of assuming only $(CH_3COOH)_2$ to exist in the benzene, it had been assumed that the compound $C_6H_5.2CH_3COOH$ were present.

Expressed experimentally, the surface-tension (and viscosity) results for this system indicate that the maximum deviation from the mixture law corresponds to just that concentration represented by 2 molecular weights of acetic acid to each molecular weight of benzene present in the mixture.

The deviations of the system *benzene-ethyl alcohol* are below 1 dyne per cm., but with a plain maximum lying close to 23% of ethyl alcohol. The compound $2(C_6H_6).C_2H_5OH$ corresponding to 22.77% of alcohol is thus evidently the one indicated.

Although from freezing-point determinations of ethyl alcohol in benzene when the concentration is low, normal values of the molecular weight are found[4] that would not prevent the above compound existing in the benzene—in fact the same reasoning would hold here as did in the preced-

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[1] *J. Chem. Soc.* **87**, 15 (1905).

[2] *Z. physik. Chem.*, **2**, 638, 715 (1888).

[3] Herz and Fischer, *Ber.*, **83**, 1138 (1905).

[4] See Beckmann, *Loc. cit.*

ing case. The existence of such a compound, then, is not inconsistent with such results.

On plotting the results of Dunstan[1] for the viscosities of this system at 25°, three points (*viz.*, 32.42, 49.09 and 54.40%) do not fall on the curve. Omitting these, and considering the deviation-composition curve as made up of the other eight concentrations, a maximum appears at 23.47% of alcohol, the nearest point to 22.77% observed. This confirms, with another physical property, the above result from surface tension.

Experiment shows here that the maximum deviation of surface tension (and viscosity) from the mixture law is at that concentration corresponding to 1 molecular weight of ethyl alcohol for every 2 molecular weights of benzene.

The deviations of the system *benzene-methyl alcohol* are negative in sign, although not large, the lower temperature leading to the larger deviations. A plot of these results (not shown here) indicates that the maximum deviation is at a concentration of 29% of methyl alcohol. The compound $C_6H_6.CH_3OH$, here, corresponds to 29.09% of methyl alcohol.

Expressed experimentally the maximum deviation from the mixture law in this case is found at a concentration of 1 mol of methyl alcohol to every mol of benzene.

The system *acetone-methyl alcohol*, as one might anticipate, is similar, in its relations to surface tension, to that of acetone-ethyl alcohol. Here, also, the observed results are *larger* than those calculated from the mixture law, and all mixtures studied at the *higher* temperature give surface tensions *larger* than that of either constituent alone, the values of the constituents having at this temperature become almost identical, *viz.*, 21.578 and 21.058, while the 50% mixture exhibits a value of 21.689.

A deviation-composition plot (not given here) shows the deviations at both temperatures to be at what is practically 50% by weight in g. of each constituent. Here, again, it can only be said that equal weights of the two constituents show a maximum, though small, deviation—another case plainly of some purely, and small, *physical* effect (corresponding to no simple chemical formula) of one constituent on the other, similar to those shown by the work of Morgan and Griggs, and by the system acetone-ethyl alcohol above.

An exceedingly interesting mixture is the *ethyl alcohol-methyl alcohol* system. Here the two substances themselves are very similar, belonging as they do to the same homologous series, with surface tensions differing by about 0.55 dyne per cm. at 0° and by only 0.25 at 50°.

Although the deviation here is very small, it is at a maximum at all temperatures at a concentration close to 50% by weight in g. of the constituents. At 0° the deviations are *positive*, *i. e.*, the observed result is

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[1] *J. Chem. Soc.*, **85**, 817 (1904).

larger than that calculated; at 30° the mixture law holds rigidly; while at 50° the deviation is *negative* and larger than the positive one at 0°. This is the first system encountered which leads to such results.

Whatever the *physical* change taking place on the mixing of the two liquids, which is at a maximum for a 50–50 g. mixture, it produces a maximum positive deviation from the law at 0°, no deviation at 30°, and a negative one at 50°. The deviations here, though small, are most certainly present, as was shown by several repetitions of the work.

For the system *benzene–phenol* fairly large deviations (nearly 3 dynes per cm.) are observed. They present a marked maximum at around 38% of benzene, which would indicate the compound $4(C_6H_5OH).3(C_6H_6)$, corresponding to 38.36% of benzene.

Bramley's viscosities and densities for this system show deviations for both properties leading to a marked maximum at 36.35% of benzene, the nearest concentration to 38.36% studied (the neighboring ones being 46.98 and 25.89), while the relative deviations in the case of density plainly point to a larger concentration than 36.35, rather than a smaller, for the real maximum. Both properties must be regarded here as confirming, and most emphatically, the conclusion from surface tension.

This is the only system, it will be observed, in which the maximum deviation has pointed to a compound that is not most simple in composition. A glance at the behavior of this system under other recognized methods of research, however, must convince one that in this case, at any rate, the compound is not at all unreasonable.

Beckmann, for example, found by the freezing-point method that the molecular weight of phenol in benzene varies from 144 in very dilute solution up to 252 in a solution containing 26.77 g. of phenol in 100 g. of benzene, which possibly indicates polymerization, and would certainly go to confirm the idea that any compound formed of solvent and solute might well be as complicated as the above.

Further, Vaubel[1] and Rothmund and Wilsmore[2] have found phenol most certainly to be polymerized when in solution in benzene, by aid of the coefficient of distribution. Although no *definite* conclusion can be drawn from them, of the results of the latter, it can be said that assuming the molecular weight to be 4 times as great in benzene as in water gives just as satisfactory a ratio as the assumption that it is twice as great.

Experimentally, here, it is found that the maximum deviation from the mixture law of surface tension, density and viscosity is found at just that composition corresponding to 4 mols of phenol to every 3 mols of benzene —a ratio no more complicated than would have to be assumed in any other method of treatment.

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[1] *J. prakt. Chem.*, [2] **67**, 476 (1903).

[2] *Z. physik. Chem.*, 41, 611 (1902).

Summary.

The results of this investigation may be briefly summarized as follows:

1. A complete survey has been made, by the drop-weight method, of the surface tensions of the ten following binary liquid mixtures, in a number of relative concentrations of constituents, at several temperatures: (1) Water-acetone, (2) acetone-ethyl alcohol, (3) phenol-acetone, (4) phenol-ethyl alcohol, (5) benzene-acetic acid, (6) benzene-ethyl alcohol, (7) benzene-methyl alcohol, (8) acetone-methyl alcohol, (9) ethyl alcohol-methyl alcohol, and (10) benzene-phenol.

2. The curves representing the variation in surface tension with concentration (*i. e.*, the so-called property-composition curves) are in general here without maxima or minima, but that of No. 5 shows a minimum, while Nos. 2 and 8 show maxima.

3. The comparison of the observed results of the various mixtures with the values calculated from the mixture law of Morgan and Griggs, using g. for the relative weights of the constituents, leads to very interesting and important results here.

According to the deviations of the directly observed results from those calculated by this mixture law, the ten systems studied in this work fall naturally into three groups:

(*a*) The systems giving observed values *smaller* than the calculated one. These include Nos. 1, 3, 4, 5, 6, 7, and 10 of the above systems.

(*b*) Those which give observed values *larger* than those calculated. These include Nos. 2 and 8.

(*c*) Those which exhibit little or no deviation from the mixture law, as No. 9, above, at 30°. This system, ethyl alcohol–methyl alcohol, is so far unique, for it exhibits a slight positive deviation at 0°, no deviation at 30°, and a small negative one at 50°.

4. The position (and magnitude) of the maximum deviation from the mixture law found when the deviation (either positive or negative) is plotted against the concentration of one constituent in g. per hundred of the mixture, divides the systems into two classes.

In one class the maximum deviation, always very small, is found for a mixture containing 50% by weight in g. of each constituent, the composition not being expressible in even molecular weights of the constituents. Such cases have already been discussed by Morgan and Griggs. These systems are Nos. 2, 8 and 9, the only explanation for their behavior being that it is due to the *physical* (not chemical) effect of the one liquid on the other, since an equal weight in g. brings about the maximum effect.

Systems of the other class, on the contrary, exhibit a maximum deviation, usually large, and at some other concentration than 50%, and which corresponds always to some simple and even relation of the molecular weights of the constituents, *i. e.*, corresponds to a definite chemical formula. The cause of this, according to the theory derived by Denison, is the actual production of a compound, for he has shown theoretically that the maximum deviation of a physical property from the mixture law must occur at that point when a compound of the constituents is present to a maximum extent, *i. e.*, where the composition of the mixture leading to the maximum deviation is of the same composition as the compound formed.

The molecular compounds found to exist in liquids by the above work on the basis of this theory (in other words, the molecular (*chemical*) compositions found empirically here to lead to the maximum deviation of the *physical* property from the mixture law) are as follows (in a number of cases the other physical properties, viscosity and density, leading to the same result):
$(CH_3)_2CO.10H_2O$; $2(C_6H_5OH).(CH_3)_2CO$; $C_6H_5OH.2(C_2H_5OH)$; $C_6H_6.2(CH_3COOH)$; $2(C_6H_6).C_2H_5OH$; $C_6H_6.CH_3OH$ and $4(C_6H_5OH).3(C_6H_6)$.

5. The compound shown to exist in the system benzene–acetic acid, *viz.*, $C_6H_6.2(CH_3COOH)$, is most interesting when considered in the light of the results of other methods, which lead to the conclusion that acetic acid is always doubly polymerized in benzene solution. These methods are such, however, as would have failed to show a combination of the solvent with the polymerized solute, even if it did exist; and hence the evidence found here pointing to such a compound is not only not inconsistent, but gives a more advanced point of view on the process we have designated in the past as a simple polymerization.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE SPECIFIC HEATS AND HEATS OF FUSION OF TRIPHENYLMETHANE, ANTHRAQUINONE AND ANTHRACENE.[1]

BY JOEL H. HILDEBRAND, ALICE D. DUSCHAK, A. H. FOSTER AND C. W. BEEBE.

Received August 13, 1917.

The following investigations were undertaken with the purpose of securing data to be used in the prediction of solubility according to the principles recently outlined by one of us.[2]

The calorimeter was similar to that described by G. N. Lewis and Merle Randall,[3] with the exception that the material was heated not in a vapor

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[1] The data herein presented, with the exception of those pertaining to anthracene, are taken from the thesis presented by Alice D. Duschak in partial fulfillment of the requirement for the degree of Master of Arts.

[2] J. H. Hildebrand, THIS JOURNAL, **28**, 1452 (1916).

[3] THIS JOURNAL, **33**, 476 (1911).